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(54) Title: INJECTION MOLDABLE CONDUCTIVE AROMATIC THERMOPLASTIC LIQUID CRYSTALLINE POLYMERIC COM- POSITIONS (57) Abstract A method for making a shaped article or a shaped article having a volume resistivity of less than 10^{-2} ohm-cm with a desired combination of properties and processibility in an injection moldable composition. In particular the shaped articles formed include injection molded bipolar plates as current collectors in fuel cell applications.		

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TITLE

INJECTION MOLDABLE CONDUCTIVE
AROMATIC THERMOPLASTIC LIQUID CRYSTALLINE
POLYMERIC COMPOSITIONS

FIELD OF INVENTION

The present invention relates to an injection moldable electrically conductive composition comprising aromatic thermoplastic liquid crystalline polymers (LCPs), electrically conductive articles made therefrom, and the injection molding process for making them. The compositions of the invention are useful in a wide variety of applications including electrochemical devices such as battery current collectors, high efficiency electromagnetic/radio frequency interference shielding, and electrostatic dissipative packaging and equipment housings. The present invention is particularly useful in fuel cells.

BACKGROUND OF THE INVENTION

15 In the current state of the art, a typical fuel cell comprises the elements shown in Figure 1. A membrane/electrode assembly (MEA), 10, comprising a membrane separator, 11, and catalyst coatings, 12, on either side thereof, and two (2) gas diffusion backing sheets, 20, are sealed by gaskets, 30, between two (2) electronically conductive graphite plates, 40. The plates often serve a multiple
20 role as current collectors conveying electrons to the external load via electrical connections not shown, as mechanical supports for the other fuel cell components, and as gas and water distribution networks via a pattern of flow fields inscribed upon the surfaces thereof, 50. Gas and water inputs and outputs are generally integral with the graphite plate, but are not shown. The graphite plates normally
25 serve as the interface between adjacent cells in a stack. The plates are known variously as current collectors, flow fields, and bipolar (or monopolar) plates. For further information, see, for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th ed. Vol. 12A, pp. 55ff, VCH, New York, 1989.

Because of its multiple role, the bipolar plate has a number of requirements to meet. The plate must have good electrical conductivity, good mechanical or structural properties and high chemical stability in the chemically reactive fuel cell environment. In addition because of its gas distribution role it must be made of a gas impermeable material and be formed with complex gas delivery channels across its surface.

35 In the current practice of the art, graphite is the material of choice for bipolar plates because of its high electrical conductivity, high strength and immunity to corrosion. However, it is brittle, expensive, and requires expensive machining to produce. The brittleness of graphite necessitates its use in ca. six (6)

mm thick slabs which adds both weight and bulk to the fuel cell, thus driving down its power density (kW/l or kW/kg) in use.

Carbon/graphite filled thermoplastic polymers have long been identified as a promising alternative to graphite in bipolar plates. In principle, conductive, reinforced thermoplastic polymer compositions can be molded directly into complex, intricate shaped components using low cost, high-speed molding processes. In addition, these more ductile materials will enable the development of new stack designs because moldable plastics offer much greater flexibility to the form of fuel cell components. Unfortunately, this potential has not been realized in the art despite numerous attempts to do so.

Electrically conductive thermoplastic polymer compositions providing volume resistivities of 10^{-3} - 10^{-2} ohm-cm are known in the art, and are of particular interest in the production of fuel cell current collectors.

US-A 3,945,844 to Nickols discloses polymer/metal composites. Polysulfone, polyphenylene sulfide, polyphenylene oxide, acrylonitrilebutadiene-styrene copolymer are combined in a variety of ways with stainless steel, silver, gold, and nickel. The amount of either metal powders or fillers or both, in the polymer/metal composite varies from 50 to 80 weight % percent. Resistivity levels as low as 10^{-3} ohm-cm are reported.

US-A-4,098,967 to Biddick et al. provides a bipolar plate formed of thermoplastic resin filled with 40-80% by volume finely divided vitreous carbon. Plastics employed in the compositions include polyvinylidene fluoride and polyphenylene oxide. The plates are formed by compression molding dryblended compositions and possess specific resistance on the order of 0.002 ohm-cm. Compression molded bipolar plates from solution blends of graphite powder and polyvinylidene fluoride are disclosed in US-3,801,374 to Dews et al. The plate so formed has a density of 2.0 g/cc and volume resistivity of 4×10^{-3} ohm-cm.

US-A-4,214,969 to Lawrance discloses a bipolar plate fabricated by pressure molding a dry mixture carbon or graphite particles and a fluoropolymer resin. The carbon or graphite are present in a weight ratio to the polymer of between 2.5:1 and 16:1. For polymer concentrations in the range of 6-28% by weight, volume resistivity is in the range of 1.2 - 3.5×10^{-3} ohm-in.

In US- A-4,339,322 to Balko et al., the physical strength of the compression molded composite of US-A-4,214,969 was improved by substituting carbon fibers or other fibrous carbon structures for some of the graphite powder. Typical composition includes 20% (by weight) polyvinylidene fluoride (PVDF), 16% (by weight) carbon fiber, and graphite powder. The dry mixture was

blended, then pressure molded into plates. The volume resistivity is in the range of 1.9×10^{-3} to 3.9×10^{-3} ohm-in at a binder/resin loading levels of 7-26 wt %.

US-A-4,554,063-85 to Braun et al. discloses a process for fabricating cathode current collectors. The current collector consists of graphite (synthetic) powder of high purity, having particle sizes in the range from 10 (micron) to 200 (micron) and carbon fibers which are irregularly distributed therein and have lengths from 1 mm to 30 mm, the graphite powder/carbon fiber mass ratio being in the range from 10:1 to 30:1. The binder/resin used is polyvinylidene fluoride. For producing the current collector, the binder is dissolved in, for example, dimethylformamide. Graphite powder and carbon fibers are then added and the resulting lubricating grease-like mass is brought to the desired thickness by spreading on a glass plate and is dried for about 1 hour at about 50°C. The plates were also formed by casting, spreading, and extrusion.

US-A-5,582,622 to Lafollette discloses bipolar plates comprising a composite of long carbon fibers, a filler of carbon particles and a fluoroelastomer.

Also known in the art is the use of metal-coated, particularly nickel-coated chopped graphite fibers to form conductive polymer compositions. In order to reduce fiber attrition by compounding, the prior art discloses employing a thermoplastic resin-impregnated bundle of nickel-coated graphite fibers which are directly injection moldable with a thermoplastic matrix resin with only a preliminary dry-blending step. See for example Kiesche, "Conductive Composites Find Their Niche," *Plastics Technology*, November 1985, P. 77ff; Murthy et al, "Metal Coated Graphite Fiber Structural Foam Composites," Fourteenth Annual Structural Foam Conference and Parts Competition, The Society of the Plastics Industry, Inc., April 1986, PP 86ff. Use of wider gates and flow channels in molding machines processing graphite fibers is disclosed for example in *International Encyclopedia of Composites*, S. Lee, ed. pp 474ff, VCH publishers, 1990. Also disclosed therein is the enhancement of conductivity realized by orientation of high aspect ratio conductive fibers in the polymer matrix during the molding process.

Methods for forming resin-impregnated graphite fibers which are also applicable to metal-coated graphite are known in the art. Some of these methods are disclosed in "Graphite Fiber Composites (Electrochemical Processing)" by J. Iroh in *Polymeric Materials Encyclopedia*, J. C. Salamone, ed., pp. 2861ff, CRC Press 1996.

The art hereinabove cited is directed to replacing pure metal or graphite components which require extensive machining to be formed into finished articles

with moldable compositions based upon thermoplastic polymer resins which require less, post-molding machining to form the finished article.

The problem in realizing the advantages of molded thermoplastic polymer parts has been related to the inverse relationship between concentration of
5 conductive filler on the one hand and processibility and mechanical properties on the other. In practice, as shown in the art hereinabove cited, quantities of conductive filler required to achieve the 10^{-2} ohm-cm resistivity goal in fuel cells result in products with limited practical utility. This is particularly true in regard to the formation of current collectors in fuel cell applications.

10 It is desirable to achieve a combination of properties and processibility in an injection moldable composition without the limitation on practical utility. Another advantage desired is the reduction in cost of forming finished articles such as current collectors in comparison to conventional methods.

SUMMARY OF THE INVENTION

15 Briefly stated, and in accordance with one aspect of the present invention, there is provided a process for fabricating a shaped article having a volume resistivity of less than 10^{-2} ohm-cm, the process comprising:

20 combining an injection moldable aromatic thermoplastic liquid crystalline polymer resin and a composition comprising nickel-coated graphite fibers impregnated with a non-liquid-crystalline thermoplastic binder resin, to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite fibers being of a length of less than 2 cm and comprising about 5 to about 50% by weight of the mixture, and the binder resin comprising about 0.1 to about 20% by weight of the graphite;

25 feeding the mixture to an injection molding machine wherein the thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold; cooling the mold to a temperature at which the thermoplastic liquid crystalline polymer in the mixture no longer flows; and, removing the molded mixture from the mold.

30 Pursuant to another aspect of the invention, there is provided a shaped article having a volume resistivity of less than 10^{-2} ohm-cm comprising about 50 to about 95% by weight of an aromatic liquid crystalline polymer about 5 to about 50% by weight of a nickel-coated graphite fiber of a length less than 2 cm, and about 0.1 to about 20% by weight with respect to the weight of the graphite fiber
35 of a non-liquid-crystalline thermoplastic binder resin.

Pursuant to another aspect of the invention, there is provided a process for fabricating an electrically conductive shaped article, the process comprising: combining an injection moldable aromatic thermoplastic liquid crystalline

polymer resin in the form of particles characterized by a mean particle size of less than 1500 micrometers with a graphite filler to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite filler being present in a concentration of about 5% to about 80% by weight of the total mixture; feeding the mixture to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold; cooling the mold to a temperature at which the resin in the mixture no longer flows; and, removing said molded mixture from the mold.

10 BRIEF DESCRIPTION OF THE FIGURES

Other features of the present invention will become apparent as the following description proceeds and upon reference to the Figures, in which:

Figure 1 is a schematic illustration of a typical fuel cell; and

15 Figure 2 is a schematic illustration of a molded bipolar plate with fluid distribution channels.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention provide a novel balance among conductivity, processibility, and structural properties. Surprisingly, it was found in the practice of the invention that injection molded plaques having excellent strength and stiffness can be produced with electrical volume resistivity in the range of 10^{-3} - 10^{-2} ohm-cm. The plaques so formed are suitable for use as current collectors in fuel cells at thicknesses in the range of about 0.2 to about 10 mm. with a preferred thickness of 1-3 mm. The combination of properties achieved by these plaques compares favorably with the machined graphite plaques which represent the current state of the art in fuel cell development. However, the present invention provides the advantage of a significantly reduced cost in the process of forming the shaped articles.

In a preferred embodiment of the present invention, the necessary balance of properties to permit direct injection molding of complex shaped articles with excellent structural properties, processibility, and volume resistivity of 10^{-2} ohm-cm or less is achieved. Despite the teachings of the prior art, and the obvious economic incentive to develop injection molded current collectors to replace the current expensive method, no satisfactory injection molded current collectors have been produced prior to the present invention. It is well known in the art that processibility and structural properties deteriorate as the amount of filler incorporated into a polymeric matrix is increased. In the art as hereinabove described, in order to achieve the volume resistivity of 10^{-2} ohm-cm or less required for practical application to fuel cells, the requisite quantity or loading of

conductive fiber and other fillers into the selected polymer matrices resulted in melt viscosities too high to permit injection molding, and such poor structural properties such as ductility, flexural strength, and impact strength that only excessively thick plaques could be employed without exhibiting structural failure in use.

The term "thermoplastic" as used herein refers to the thermoplastic liquid crystalline polymer resin suitable for the practice of the present invention that is melt processible according to conventional methods known in the art for melt processing plastics such as screw extrusion and injection molding.

In the present invention, the easy moldability of aromatic thermoplastic liquid crystalline polymers allows formation of conductive shaped articles of complex shape and thin walls and sufficient loading of conductive fillers affords excellent conductivity. The excellent chemical resistance of molded aromatic thermoplastic liquid crystalline polymers combined with the as-molded complex shapes makes the process of the present invention particularly well-suited for the fabrication of bipolar plates useful in fuel cells.

Furthermore, an embodiment of the present invention provides an injection moldable composition comprising an injection moldable aromatic thermoplastic liquid crystalline polymerthermoplastic thermoplastic liquid crystalline polymer resin, and a conductive graphite filler, which is fed to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymerthermoplastic thermoplastic liquid crystalline polymer is melted, the graphite filler is dispersed within the polymer melt so formed during the advance of the injection molding screw, and the molten resin composition is fed to a mold wherein it is solidified and then ejected as a solid shaped article.

In a preferred embodiment of the present invention, the ingredients of the composition are dry mixed prior to feeding. Dry mixing may be accomplished by any convenient means such as tumbling. Preferably, the composition also comprises a dispersing agent, and such other additives as may be desired or required to improve processibility or end-use properties.

Aromatic thermoplastic liquid crystalline polymers suitable for the practice of the present invention include those described in U.S. Patents 3,991,013; 3,991,014; 4,011,199; 4,048,148, 4,075,262;4,083,829; 4,118,372;4,122,070; 4,130,545; 4,153,779; 4,159,365;4,161,470; 4,169,933; 4,184,996;4,189,549; 4,219,461;4,232,143;4,232,144; 4,245,082; 4,256,624; 4,269,964; 4,272,625; 4,370,466;4,383,105;4,447,592;4,522,974;4,617,369;4,664,972;4,684,712; 4,727,129;4,727,131;4,728,714;4,749,769;4,762,907;4,778,927;4,816,555; 4,849,499;4,851,496;4,851,497;4,857,626;4,864,013;4,868,278;4,882,410;

4,923,947; 4,999,416; 5,015,721; 5,015,722; 5,025,082; 5,086,158; 5,102,935;
5,110,896; 5,143,956.

Useful aromatic thermoplastic liquid crystalline polymers include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines.

5 Especially useful are aromatic thermoplastic liquid crystalline polymers that are polyesters or poly(ester-amides). It is also preferred in these polyesters and poly(ester-amides) that at least about 50 %, more preferably about 75% of the bonds to ester or amide groups, i.e., the free bonds of $-C(O)O-$ and $-C(O)NR^1-$ where R^1 is hydrogen or hydrocarbyl, be to carbons atoms which are part of
10 aromatic rings.

In a preferred embodiment of the present invention, the polyesters or poly(ester-amides) are made from monomers such as one or more aromatic dicarboxylic acid such as isophthalic acid, terephthalic acid, 4,4-bibenzoic acid, 2,6-naphthalene dicarboxylic acid, one or more aromatic dihydroxy compounds such
15 as hydroquinone, a substituted hydroquinone such as methylhydroquinone, t-butylhydroquinone, and chlorohydroquinone, resorcinol, 4,4'-biphenol, 2,6-naphthalenediol, and 2,7-naphthalenediol, one or more aromatic hydroxyacids such as 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, and 6-hydroxy-2-naphthoic acid and (in the case of poly(ester-amides)) one or more aromatic diamines such
20 as p-phenylenediamine or m-phenylenediamine.

Included within the definition herein of an aromatic thermoplastic liquid crystalline polymer is a blend of 2 or more aromatic thermoplastic liquid crystalline polymers, or a blend of an aromatic thermoplastic liquid crystalline polymer with one or more non-aromatic thermoplastic liquid crystalline polymers
25 wherein the aromatic thermoplastic liquid crystalline polymer is the continuous phase.

In one embodiment of the present invention, an aromatic thermoplastic liquid crystalline resin is combined with a conductive, metal-coated, preferably nickel-coated, graphite fiber, formed into pellets by the adhesive action of a
30 thermoplastic resin binder. In the process of the invention, the aromatic thermoplastic liquid crystalline resin is preferably dry mixed, as by tumbling, with the metal-coated graphite fiber pellets to form a coarse homogeneous mixture. The mixture is fed to the feed throat of an injection molding machine and the resins melt as the resin mixture is conveyed along the flights of the screw while
35 the action of the screw causes the fibers to disperse within the aromatic thermoplastic liquid crystalline resin melt. The molten dispersion is fed to a mold in which the melt hardens to form a shaped article which is then ejected from the mold.

In a preferred embodiment of the present invention, the shaped article formed according to the process of the invention is a bipolar plate having fluid-flow channels molded into the surface thereof being suitable for use in hydrogen or direct methanol fuel cells with little or no post molding finishing required.

5 Suitable conductive fibers are graphite fibers, preferably metal coated graphite fibers, and most preferably nickel-coated graphite fibers. The length of the graphite fibers is less than ca. 1", preferably 0.125-0.5", and the diameter is in the range of about 5 to about 40 micrometers, preferably about 5 to about 15 micrometers. While any degree of metal coating is an improvement over
10 uncoated graphite fibers, a metal coating level of about 20% to about 70% by weight of the total weight of the metal-coated fiber plus thermoplastic resin binder is preferred while approximately 45%-60% is most preferred. Because of the combination of chemical stability, low density, excellent performance, and low cost, nickel is the preferred coating metal.

15 In the preferred embodiment of the present invention, nickel-coated graphite fibers are present in the composition of the invention at concentrations in the range of about 5% to about 50%, preferably about 10% to about 40% by weight.

In the preferred embodiment of the invention, the thermoplastic resin
20 binder represents about 0.1 to about 20% by weight, preferably about 5 to about 15% by weight of the total nickel-coated graphite fiber composition prior to mixing into the composition of the invention. The most preferred polymeric binder is a low melting polyamide copolymer or terpolymer.

The following discussion is provided for the purpose of illustrating a
25 preferred embodiment of the invention and not for limiting same. Because of limitation in both residence time and screw design in injection molding machines, it is believed that considerable benefit accrues when the time available for dispersion of the metal-coated graphite fiber in the molten resin matrix is maximized. Pursuant to that goal, it is preferable that the thermoplastic binder
30 resin become fluid at a lower temperature than that at which the aromatic thermoplastic liquid crystalline resin melts, thus, ensuring that the dispersion of the fiber will be well-under way while the aromatic thermoplastic liquid crystalline resin is melting.

The thermoplastic binder resin may or may not be useful as a dispersing
35 agent. Alternatively, it may be desirable to add a dispersing agent to the composition.

The thermoplastic resin binder may be deposited on to the fibers of the invention by any means known in the art including melt impregnation, solution

impregnation, in-situ polymerization of dispersed monomer, and electrodeposition. No one means, known in the art, is preferred over another.

Aromatic thermoplastic liquid crystalline polymers are manufactured and commercially available as pellets ca. 0.125" in diameter. It is found surprisingly
5 in the practice of the present invention that conductivity is improved when aromatic liquid crystalline pellets are subject to size attrition to form particles having a mean particle size of less than 1500 μm , preferably less than 1000 μm , prior to combining with a conductive graphite filler.

In a further embodiment of the present invention, an aromatic
10 thermoplastic liquid crystalline resin having a mean particle size of less than 1500 μm , preferably less than 1000 μm , is combined with a conductive graphite filler. In the process of the present invention, the aromatic thermoplastic liquid crystalline resin is preferably dry mixed, as by tumbling, with the graphite filler to form a coarse homogeneous mixture. The mixture is fed to the feed throat of an
15 injection molding machine and the aromatic thermoplastic liquid crystalline polymer melts as it is conveyed along the screw flights, and the action of the screw causes the filler to disperse within the aromatic thermoplastic liquid crystalline resin melt. The molten dispersion is fed to a mold in which the melt hardens to form a shaped article which is then ejected from the mold.

20 The conductive graphite filler is present in the composition of the invention at concentrations in the range of about 5% to 80%, preferably about 30 to 70% by weight, most preferably 30 to 50% by weight. Suitable graphite fillers include powdered graphite, such as Thermocarb[®] graphite powder from Conoco, Inc., more preferably a graphite fiber, such as pitch based graphite fibers available
25 from Conoco, Inc., still more preferably, a metal-coated graphite fiber, most preferably a nickel-coated graphite fiber such as hereinabove described.

Attrition of the particle size of the aromatic thermoplastic liquid crystalline resin pellets may be accomplished according to the following procedure: A rotary cutter or grinder, such as an ABBE cutter (Model Number:
30 000 Laboratory Rotary Cutter serial no. 49491, Abbe Engineering Company, Brooklyn, NY 11211), is equipped with a metal screen having holes 0.060 inches (0.15 cm) in diameter. A beaker is filled with aromatic thermoplastic liquid crystalline resin pellets and immersed in liquid nitrogen and held for ca. two minutes after the liquid has stopped boiling. After immersion in the liquid
35 nitrogen, the beaker of pellets is removed and the pellets fed to the moving blades of the cutter. Frequent clearing of the cutter is necessary because only ca. 50% of the resin pellets are actually effectively cut, leaving the cutter

contaminated with a buildup of warmed pellets. The residual pellets may be recycled to the cutter after further immersion in liquid nitrogen.

It is found in the practice of the invention that when pellets of nickel-coated graphite of ca. 3.2 mm in size and larger are combined with the powdered thermoplastic liquid crystalline resin of less than 1.5 mm in size, and particularly less than 1.0 mm in size, some separation of components occurs during feeding to the injection molding machine. Some loss in homogeneity within and among resulting molded parts may result. It is therefore, desirable to take additional measures to ensure that the components remain well mixed on a macroscopic scale while feeding. This may be accomplished by employing nickel-coated graphite fibers having a smaller aspect ratio so that the pellets formed therefrom may have smaller dimensions. Another method is to adapt stuffer box technology known for feeding extruders to feeding injection molding machines. Still another method is to maintain mixing even as the material is fed into the screw of the injection molding machine. These, and other methods known in the art, may be employed, alone or in combination, to maintain homogeneity in the embodiments of the invention in which a considerable size mismatch occurs in the materials being fed.

To improve the homogeneity of the dispersion of the conductive filler into the aromatic thermoplastic liquid crystalline polymer, it may be desirable to incorporate into the compositions, formed according to the process of the present invention, a dispersing aid. The dispersing aid can be of any type known in the art to be effective in enhancing the dispersibility of metal or graphite fibers in polymeric melts. The dispersing aid may be crystalline or non-crystalline, and may be normally liquid at room temperature. In the present invention, the dispersing aid is required to be immobile in the composition at room temperature. For a liquid dispersing aid, the liquid must be immobilized by adsorption or absorption onto the fiber. Suitable dispersing aids include low molecular weight species such as fatty acids, silanes, difunctional oligomers and so forth. Dispersing aids may also be polymeric in nature, such as the thermoplastic resin binder incorporated into the nickel-coated graphite fiber pellets which are preferred for use in the present invention. The choice of dispersing aid is also governed by compatibility with the matrix polymer. Compatibility is largely an empirical determination. A compatible dispersing aid is one that will cause the fiber to disperse within the polymeric matrix, whereas a non-compatible dispersing aid doesn't cause dispersion but instead causes the fiber to form isolated clumps.

The composition of the present invention may contain such other additives as may be required to improve processibility or properties. In particular, in the practice of the present invention the addition of ca. 5-20% by weight carbon black to the composition provides a desirable improvement in conductivity with
5 relatively small degradation of processibility or structural properties. Preferred is a highly structured carbon black such as Printex XE from Degussa, Black Pearl 2000 from Cabot or Ketjenblack EC300J from Akzo Nobel.

It is important in the present invention that the ingredients be subject to as little shearing force as possible because shearing force associated with melt
10 mixing and extrusion normally performed to form filled polymeric compositions results in degradation of the conductivity performance. Thus all steps in the process of the present invention should be performed with an eye toward keeping shear forces low.

While any means known in the art for mixing at low shear is suitable, in
15 the practice of the present invention simple dry tumbling of the ingredients works well. In the process of the present invention, the mixture so formed is fed to a conventional injection molding machine where the polymers undergo melting, and are conveyed to the mold followed by cooling and ejection. The injection moldable composition of the invention is suitable for use on any injection molding
20 machine which provides the limited melt shear necessary for dispersion of the fibers in the matrix polymer melt. While a wide range of mold and runner geometries may be employed, it is found advantageous to reduce the degree of shear to which the melt is subject by employing large diameter gates and runners.

For the purposes of the present invention, premixing the dry or unmelted
25 ingredients at low shear includes simply feeding the separate ingredients directly to the feed hopper of the injection molding machine such as by employing controlled rate-of-weight-loss feeders where the mixture is made *in situ* within the feed throat of the injection molding machine.

This invention enables the production of thinner (e.g., all the molded
30 samples in the Examples section below are 1/8" (~3.2 mm) thick, the target thickness range for bipolar plates in fuel cells is about 1 to about 3 mm.), lighter, and lower cost conductive articles while significantly reducing or eliminating the need for the costly machining steps employed at the current state of the art. The articles of the invention exhibit volume resistivity of ca. 10^{-2} ohm-cm or less. In
35 the preferred embodiment, current collectors having complex gas flow networks, highly suitable for use in fuel cells may be directly injection molded, requiring little or no finishing prior to use.

Reference is now made to the following specific embodiments for the purpose of illustrating the invention and for limiting same.

EXAMPLES

A description of the materials employed in the examples hereinbelow cited
5 is provided in Table 1.

TABLE 1
Description of Materials

Name	Description	Manufacturer	Resin Melting Point	Product Form
Zenite® HX8000	Aromatic liquid crystalline Aromatic Polyester,	DuPont Company, Wilmington DE	~240-260°C	Resin pellets
PP1-1204-Ni60 and PP1-1208-Ni60	Resin Impregnated Nickel-coated Graphite Fibers (with 60w% nickel coating)	Composite Materials, LLC, Mamaroneck, NY USA	~232°C	1/4" and 1/2" fibers in pellet form- pellet diameter (~1/16")-12000 fibers per pellet (~7-8 micrometer), typical fiber aspect ratio - 300-1000
PP1-1204-NiCu40	Resin Impregnated Nickel-Copper Coated Graphite Fibers with ~35% copper and about 5% nickel	Composite Materials, LLC, Mamaroneck, NY USA	~232°C	1/4" and 1/2" fibers in pellet form- pellet diameter (~1/16")-12000 fibers per pellet (~7-8 micrometer), typical fiber aspect ratio - 300-1000
Thermocarb® CF300	Graphite Powder	Conoco, Ponca City, OK USA		Particle size 45 -300 micrometer
Mesophase pitch- based graphite fiber	Graphite Fiber	Conoco, Ponca City, OK USA		Fiber length ca. 1mm

The nickel-coated graphite fibers were supplied in the form of 12,000 fiber pellets containing 5-15 wt-% of a low melting polyamide binder with a melting point 232°C. The fibers further consisted of 60% by weight nickel and 25-35% by weight graphite. The fibers were provided in 1/4" and 1/2" lengths.

- 5 Drying conditions applicable to the materials cited in the examples cited hereinbelow are as shown in Table 2.

TABLE 2

Drying Conditions

Material	Drying Temperature (°C)	Duration at Temperature (hours)	Other
Zenite® HX8000	105	=12	hopper dryer under N2
Nickel-coated graphite fibers	220	=4	oven dried under N2
Thermocarb® CF300	—	—	used as received
Mesopitch Graphite Fibers			used as received

10

In all examples injection molding was effected utilizing a 180 ton injection molding machine (Nissei Manufacturing, Nagano, Japan). The parts formed were 3"x 6"x 0.125" and 4"x4"x0.125" flat plaques.

- 15 All the volume resistivity measurements were done on the flat molded plaques using a four point probe (ref: "Electrical Resistivity Measurements of Polymer Materials" by A. R. Blythe in Polymer Testing 4 (1984) 195-200). Six (6) measurements were done on each side of the sample and the average of the measurement is reported as the volume conductivity number in the following examples.

20

EXAMPLE 1

2730 g of HX8000 (dried at 105°C for 12 hrs) was dry blended by tumbling with 910 g ach of 1/4" and 1/2" long Nickel coated Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

- 25 Melt Temperature: 320°C
 Mold Temperature: 30-70°C
 Injection pressure: 703 kg/cm²
 Injection speed: 2.5-5 cm/sec
 Screw Speed: 50-75 RPM
 Set Injection time (max): 14 sec
 Set Curing Time (max): 18 sec
 Set Cycle Start Time (max): 1 sec
 Back Pressure: 0 kg/cm²
- 30

The volume resistivity was found to be about 2.0×10^{-3} ohm-cm.

Reference is now made to Figure 2 which shows a molded bipolar plate of Example 1 with fluid distribution channels, 100, molded therein.

EXAMPLE 2

5 3185 g of HX8000 was dry blended with 682 g each of 1/4" long and 1/2" long Nickel coated Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

	Melt Temperature:	320°C
	Mold Temperature:	80-87°C
10	Injection pressure:	492 kg/cm ²
	Injection speed:	2.5-5 cm/sec (variable in cycle)
	Screw Speed:	50-75 RPM
	Set Injection time (max):	14 sec
	Set Curing Time (max):	18 sec.
15	Set Cycle Start Time (max):	1 sec.
	Back Pressure:	0 kg/cm ²
	Shot Size:	54%

The volume resistivity was found to be about 1.0×10^{-2} ohm-cm.

COMPARATIVE EXAMPLE 1

20 2730 g of HX8000 and 6370 g of Thermocarb CF300 graphite Powder were melt compounded under vacuum in a Welding Engineers (King of Prussia, PA) 20 mm counter-rotating twin screw extruder. The polymer was fed into the first zone while the graphite was fed down stream after the polymer had melted. Screw speed was 125-150 rpm, and throughput was ca. 4550-6800 g. Die temperature was ca. 290-300°C. The extruded strand was chopped into ca. 0.125" pellets.

25 About 1360 g of formulation thus compounded was dryblended first with 910 g of additional HX8000 and then dry blended with 455 g each of 1/2" long and 1/4" long Nickel Graphite Fibers pellets. The blended mixture was injection molded at the following conditions.

	Melt Temperature:	320°C
	Mold Temperature:	70-80°C
	Injection pressure:	984 kg/cm ²
	Injection speed:	2.5-5 cm/sec (variable in cycle)
35	Screw Speed:	50-75 RPM
	Set Injection time (max):	14 sec
	Set Curing Time (max):	18 sec

Set Cycle Start Time (max): 1 sec

Back Pressure: 0 kg/cm²

The volume resistivity was found to be about 2.5×10^{-2} ohm-cm.

COMPARATIVE EXAMPLE 2

- 5 2730 g dryblended HX8000 with 1820 g of Copper (on Nickel coating) coated (about 45 wt. % metal on fiber basis) graphite Fibers pellets. Each pellet contains 12000 fibers held together with a nylon proprietary based binder (5-15 wt %-fiber basis).

The blended mixture was injection molded at the following conditions.

- 10 Melt Temperature: 320°C
 Mold Temperature: 70-76°C
 Injection pressure: 703 kg/cm²
 Injection speed: 2.5-5 cm/sec
 Screw Speed: 50-75 RPM
- 15 Set Injection time (max): 14 sec
 Set Curing Time (max): 18 sec
 Set Cycle Start Time (max): 1 sec
 Back Pressure: 0 kg/cm²

The volume resistivity was found to be about 2.3×10^{-2} ohm-cm.

20 EXAMPLES 3-6 AND COMPARATIVE EXAMPLES 3-6

- In Examples 3-6 and Comparative Examples 3-6 a comparison is drawn between the volume resistivity of flat plates molded from compositions comprising 3200 μ m (0.125 inch) aromatic thermoplastic liquid crystalline resin pellets as received from the manufacturer, and compositions comprising 951 μ m
- 25 mean particle size cryogenically ground pellets.

- The thermoplastic liquid crystalline resin powder was made by filling a 250 ml plastic beaker provided with holes in the bottom and fitted with a wire handle with ca. 1/8" (3.2 mm) resin pellets, followed by immersion of the thus filled beaker into a large bath of liquid nitrogen contained in a Dewar flask. The
- 30 beaker was kept in the liquid nitrogen for a period of two minutes following the cessation of active boiling of the liquid nitrogen. An ABBE rotary cutter provided with a metal screen having holes 0.060" (1.5 mm) was started with the hopper slide closed. Wearing a face shield and thermally insulated gloves, the resin filled beaker was removed from the liquid nitrogen and its contents dumped into the
- 35 feed hopper of the cutter. The slide was opened and the pellets fell into the blades. In any given run, only about 50% of the pellets fed were ground up. It was therefore necessary to stop every third or fourth run to clean out residual, now-warmed pellets and recycle them through the process.

Size determination were done using a laser diffraction method employing a Malvern Mastersizer X manufactured Malvern Instruments Ltd, Malvern, UK.

Whether powdered or in pellet form, the Zenite 8000 thermoplastic liquid crystalline resin (available in 3.2 mm pellets from DuPont, Wilmington, DE) was dried for 12 hours at 105°C under nitrogen.

In all cases a 180 ton injection molding machine (Nissei Mftg., Nagano, Japan) was employed to form plaques of dimensions 3" x 6" x 0.125" or 4" x 4" x 0.125".

Results are tabulated in Table 3.

10

EXAMPLE 3

700 grams of the thermoplastic liquid crystalline resin powder was tumble-blended with 1300 grams of Thermocarb® CF300 graphite powder, the blend then fed immediately to the injection molding machine and molded under the following injection molding conditions:

15	Melt Temperature	320°C
	Mold Temperature	150°C
	Injection Pressure	1125 kg/cm ²
	Injection Speed	5 cm/sec (variable in cycle)
	Screw Speed	125-140 RPM
20	Set Injection Time (max)	30.0 sec.
	Set Curing time (max)	60.0 sec.
	Set Cycle Start time (max)	1 sec.
	Back Pressure	0 kg/cm ²
	Shot size	~40-60%.

25

EXAMPLE 4

The materials and conditions of Example 3 were repeated except that 600 grams of thermoplastic liquid crystalline resin powder were combined with 1400 grams of Thermocarb® CF300.

EXAMPLE 5

30

1050 grams of thermoplastic liquid crystalline resin powder was tumble blended with 1290 grams of Thermocarb® CF300 graphite powder and 660 grams of mesophase pitch based graphite fibers. The combination was fed immediately to an injection molding machine, and injection molded under the following injection molding conditions:

35	Melt Temperature	320°C
	Mold Temperature	150°C
	Injection Pressure	1335 kg/cm ²
	Injection Speed	2.5-5 cm/sec (variable in cycle)

	Screw Speed	100-125 RPM
	Set Injection Time (max)	25.0 sec.
	Set Curing time (max)	45.0 sec.
	Set Cycle Start time (max)	1 sec.
5	Back Pressure	0 kg/cm ²
	Shot size	~40-60%.

EXAMPLE 6

The materials and procedures of Example 5 were employed except that 990 grams of the graphite fiber was employed.

10

COMPARATIVE EXAMPLE 3

700 gms of dried Zenite 8000 pellets was dryblended by tumbling with 1300 gm of Thermocarb graphite powder CF300. The blended mixture was directly injection molded according to the following injection molding conditions:

	Melt Temperature	320°C
15	Mold Temperature	150°C
	Injection Pressure	1195 kg/cm ²
	Injection Speed	2.5-5 cm/sec (variable in cycle)
	Screw Speed	100-125 RPM
	Set Injection Time (max)	20.0 sec.
20	Set Curing time (max)	30.0 sec.
	Set Cycle Start time (max)	1 sec.
	Back Pressure	0 kg/cm ²
	Shot size	~40-60%

COMPARATIVE EXAMPLE 4

25 The materials and procedures of Comparative Example 3 were employed except that 600 grams of dried Zenite 8000 pellets was combined with 1400 grams of Thermocarb CF300.

COMPARATIVE EXAMPLE 5

30 1050 gms of dried Zenite 8000 pellets was dryblended by tumbling with 1290 gm of Thermocarb graphite powder CF300 and 660 gm of pitch based graphite fibers. The blended mixture was injection molded under the following injection molding conditions:

	Melt Temperature	320°C
	Mold Temperature	150°C
35	Injection Pressure	1195 kg/cm ²
	Injection Speed	2.5-5 cm/sec(variable in cycle)
	Screw Speed	100-125 RPM
	Set Injection Time (max)	20.0 sec.

Set Curing time (max)	30.0 sec.
Set Cycle Start time (max)	1 sec.
Back Pressure	0 kg/cm ²
Shot size	~40-60%.

5

COMPARATIVE EXAMPLE 6

The materials and procedures of Comparative Example 5 were repeated except that 1050 grams of Zenite were combined with 990 grams of Thermocarb CF300 and 990 grams of pitch based graphite fibers.

10

TABLE 3

Volume Resistivity in Examples 4-8 and Comparative Examples 4-8

Example	Vol. Resist (4pt. Probe) <i>ohm.cm</i>
Ex. 3	0.18
Comp. Ex. 3	0.21
Ex. 4	0.12
Comp. Ex. 4	0.15
Ex. 5	0.18
Comp. Ex. 5	0.27
Ex. 6	0.18
Comp. Ex. 6	0.32

IT IS CLAIMED:

1. A process for fabricating a shaped article having a volume resistivity of less than 10^{-2} ohm-cm, the process comprising:
 - combining an injection moldable aromatic thermoplastic liquid
 - 5 crystalline polymer resin and a composition comprising nickel-coated graphite fibers impregnated with a non-liquid-crystalline thermoplastic binder resin, to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite fibers being of a length of less than 2 cm and comprising about 5 to about 50% by weight of the mixture, and the
 - 10 binder resin comprising about 0.1 to about 20% by weight of the graphite;
 - feeding the mixture to an injection molding machine wherein the thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold;
 - cooling the mold to a temperature at which the thermoplastic liquid
 - 15 crystalline polymer in the mixture no longer flows; and,
 - removing the molded mixture from the mold.
2. The process of Claim 1, wherein the nickel coated graphite fibers comprise about 10- about 40% by weight of the total composition.
3. The process of Claim 1, wherein the nickel-coated graphite fibers are
- 20 of a diameter in the range of about 5- about 15 micrometers.
4. The process of Claim 1, wherein the nickel-coated graphite fibers have a nickel-coating representing about 45%- about 60% or a total weight of the nickel-coated graphite fibers.
5. The process of Claim 1, wherein the aromatic thermoplastic liquid
- 25 crystalline polymer is a polyester or a poly(ester-amide).
6. The process of Claim 5, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.
7. The process of Claim 6, wherein at least 75% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.
- 30 8. The process of Claim 1, wherein the binder resin comprises about 5%- about 15% by weight of the graphite.
9. A shaped article having a volume resistivity of less than 10^{-2} ohm-cm comprising about 50- about 95% by weight of an thermoplastic aromatic liquid crystalline polymer and about 5% to about 50% by weight of a
- 35 nickel- coated graphite fiber of a length less than 2 cm, and a non-liquid-crystalline thermoplastic resin at a concentration of about 0.1%- about 20% by weight with respect to the weight of the graphite.

10. The shaped article of Claim 9, wherein the shaped article comprises about 10% to about 40% by weight of the nickel-coated graphite fiber.

11. The shaped article of Claim 9, wherein the nickel-coated graphite fiber is of a diameter in the range of about 5 to about 15 micrometers.

5 12. The shaped article of Claim 9, wherein the nickel-coating represents about 45 to about 60% of the total weight of the nickel-coated graphite fiber.

13. The shaped article of Claim 9, wherein the aromatic thermoplastic liquid crystalline polymer is a polyester or a poly(ester-amide).

10 14. The shaped article of Claim 13, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms that are part of aromatic rings.

15. The shaped article of Claim 14 wherein at least 75% of the bonds to ester or amide groups are to carbon atoms that are part of aromatic rings.

16. The shaped article of Claim 9, wherein the binder resin comprises about 5% to about 15% by weight of the graphite.

15 17. The shaped article of Claim 9, comprising a form of a bipolar plate.

18. The shaped article of Claim 17, wherein the bipolar plate has a thickness in the range of about 0.1 to about 10 mm.

19. The shaped article of Claim 18, wherein the bipolar plate thickness is in the range of about 1 to about 3 mm.

20 20. The shaped article of Claim 17, further comprising fluid distribution channels inscribed upon the surface thereof.

21. A process for fabricating an electrically conductive shaped article, the process comprising:

25 combining an injection moldable aromatic thermoplastic liquid crystalline polymer resin in the form of particles characterized by a mean particle size of less than 1500 micrometers with a graphite filler to form a mixture at a temperature below the melting point of the thermoplastic liquid crystalline polymer resin, the graphite filler being present in a concentration of about 5% to about 80% by weight of the total mixture;

30 feeding the mixture to an injection molding machine wherein the aromatic thermoplastic liquid crystalline polymer resin is melted and fed in the molten state to a mold;

cooling the mold to a temperature at which the resin in the mixture no longer flows; and,

35 removing said molded mixture from the mold.

22. The process of Claim 21, wherein the thermoplastic liquid crystalline polymer resin particles are characterized by a mean particle size of less than 1000 micrometers.

23. The process of Claim 21, wherein the graphite filler comprises a graphite fiber.

24. The process of Claim 23, wherein the graphite filler comprises a fiber of a length less than 2 cm.

5 25. The process of Claim 23, wherein the graphite fiber further comprises a metal coating.

26. The process of Claim 25, wherein the metal coating is a nickel coating.

10 27. The process of Claim 26, wherein the nickel coated graphite fiber comprises about 10% to about 40% by weight of the total composition.

28. The process of Claim 26 wherein the nickel-coated graphite fiber are of a diameter in the range of 5 to 15 micrometers.

29. The process of Claim 26, wherein the nickel-coating represents about 45% to about 60% of the total weight of the nickel-coated graphite fiber.

15 30. The process of Claim 21, wherein the aromatic thermoplastic liquid crystalline polymer is a polyester or a poly(ester-amide).

31. The process of Claim 30, wherein at least 50% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

20 32. The process of Claim 31, wherein at least 75% of the bonds to ester or amide groups are to carbon atoms which are part of aromatic rings.

33. The process of Claim 26, wherein the nickel-coated graphite fiber further comprises a non-liquid-crystalline thermoplastic binder resin.

34. The process of Claim 33, wherein the binder resin comprises about 0.1% to 20% by weight of the graphite.

25 35. The process of Claim 34, wherein the binder resin comprises about 5% to about 15% by weight of the graphite.

36. A shaped article formed according to the process of Claim 1.

37. A shaped article formed according to the process of Claim 21.

38. The shaped article of Claim 36 comprising a form of a bipolar plate.

30 39. The shaped article of Claim 37 comprising a form of a bipolar plate.

40. The shaped article of Claim 36 further comprising fluid distribution channels inscribed upon the surface thereof.

41. The shaped article of Claim 37 further comprising fluid distribution channels inscribed upon the surface thereof.

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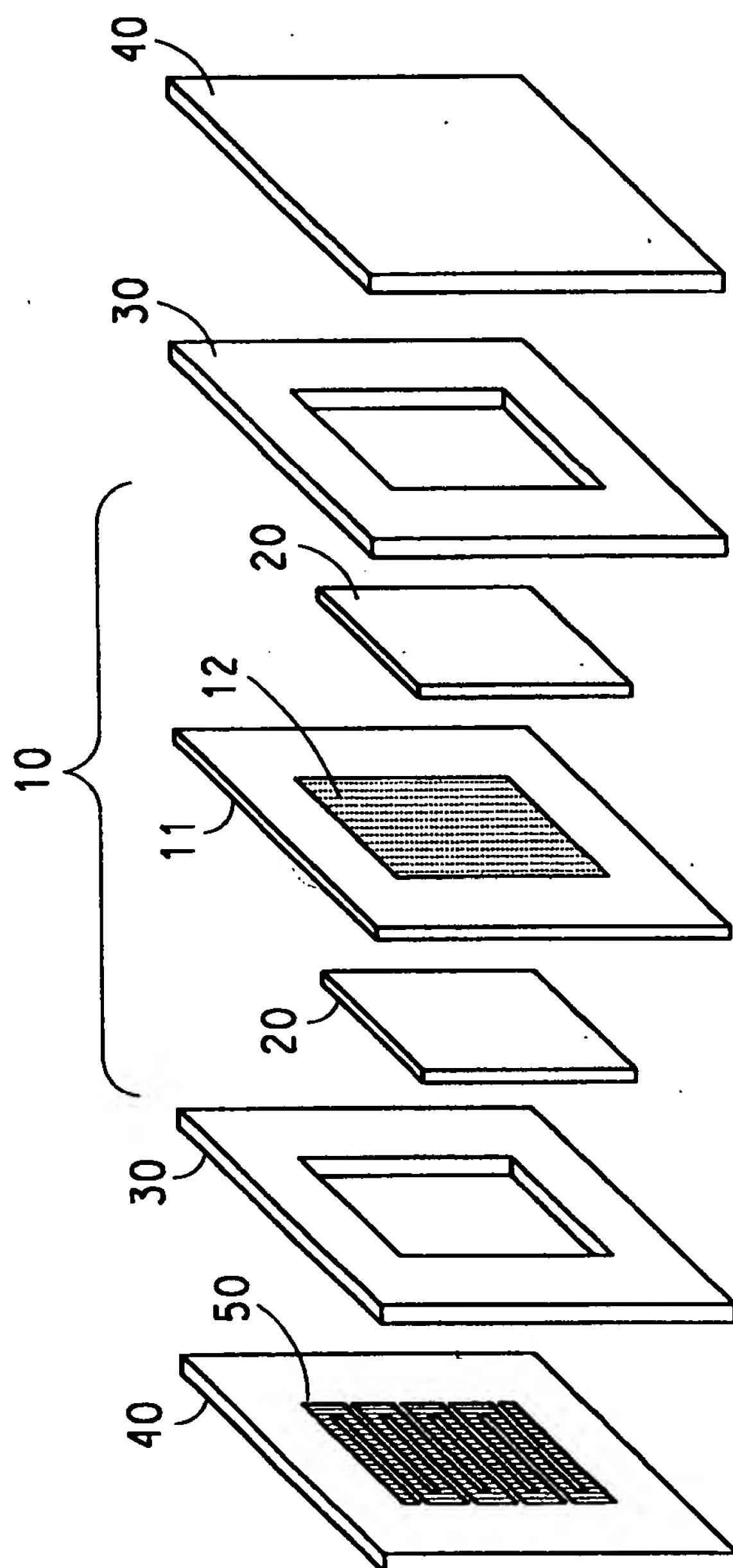


FIG. 1

2/2

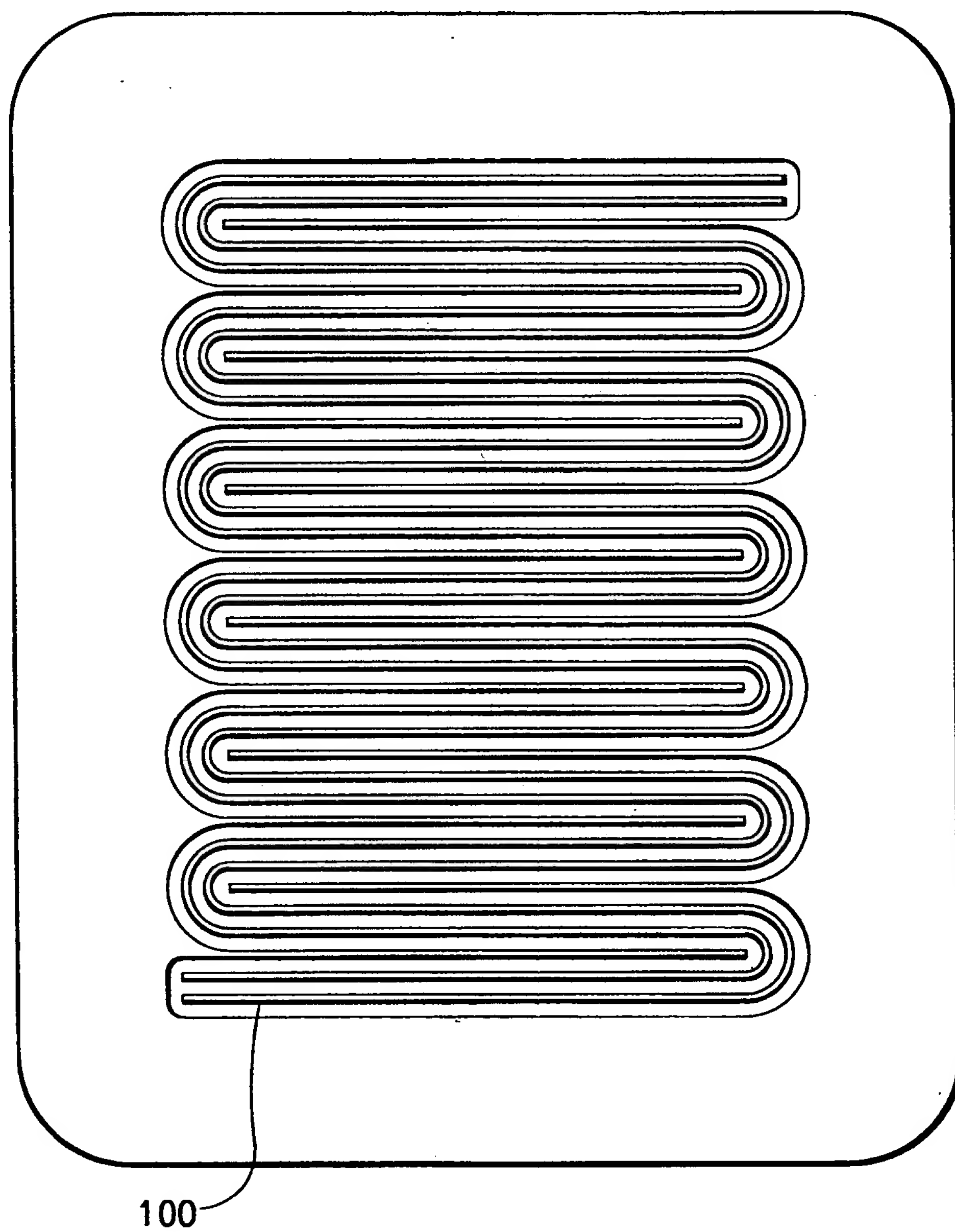


FIG. 2

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 00/01159

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01B1/20 C08K3/04 H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01B C08K H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 214 969 A (LAWRENCE RICHARD J) 29 July 1980 (1980-07-29) cited in the application the whole document	1-41
A	EP 0 485 991 A (MATRIX SCIENCE CORP) 20 May 1992 (1992-05-20) page 2, column 2, line 40 - line 43	1-41
A	EP 0 572 911 A (SUMITOMO CHEMICAL CO) 8 December 1993 (1993-12-08) the whole document	1-41
A	US 5 292 831 A (EARLS JIMMY D ET AL) 8 March 1994 (1994-03-08) the whole document	1-41
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 May 2000

Date of mailing of the international search report

31/05/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/01159

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 516 837 A (GOTOH YOSHIHISA ET AL) 14 May 1996 (1996-05-14) the whole document	1-41

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/01159

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4214969 A	29-07-1980	DE 2951964 A	17-07-1980
		FR 2445861 A	01-08-1980
		GB 2039954 A, B	20-08-1980
		IT 1126670 B	21-05-1986
		JP 1504686 C	13-07-1989
		JP 55115980 A	06-09-1980
		JP 63049755 B	05-10-1988
EP 0485991 A	20-05-1992	DE 69124467 D	13-03-1997
		DE 69124467 T	15-05-1997
		JP 5205817 A	13-08-1993
EP 0572911 A	08-12-1993	JP 6207083 A	26-07-1994
		US 5428100 A	27-06-1995
US 5292831 A	08-03-1994	AU 638690 B	08-07-1993
		AU 4851390 A	26-07-1990
		BR 9000162 A	23-10-1990
		CA 2007798 A	17-07-1990
		EP 0379057 A	25-07-1990
		JP 2275872 A	09-11-1990
		SG 52478 A	28-09-1998
		US 5463091 A	31-10-1995
		US 5736620 A	07-04-1998
		US 5266660 A	30-11-1993
		US 5270404 A	14-12-1993
		US 5270405 A	14-12-1993
US 5516837 A	14-05-1996	JP 2919636 B	12-07-1999
		JP 4342763 A	30-11-1992
		JP 2923077 B	26-07-1999
		JP 4351662 A	07-12-1992
		JP 4351663 A	07-12-1992
		JP 2981301 B	22-11-1999
		JP 4351664 A	07-12-1992
		JP 4351665 A	07-12-1992
		US 5312866 A	17-05-1994
		US 5571875 A	05-11-1996
		US 5514748 A	07-05-1996
		DE 69026209 D	02-05-1996
		DE 69026209 T	22-08-1996
		DE 69032416 D	16-07-1998
		DE 69032416 T	05-11-1998
		EP 0430640 A	05-06-1991
		EP 0633294 A	11-01-1995
		EP 0812885 A	17-12-1997
		JP 2535666 B	18-09-1996
		JP 4175373 A	23-06-1992
		KR 9405648 B	22-06-1994
		JP 2930564 B	03-08-1999
		JP 10081822 A	31-03-1998
		JP 2714544 B	16-02-1998
		JP 8104811 A	23-04-1996
		KR 9405649 B	22-06-1994
		KR 9405650 B	22-06-1994